UTADIENE FROM THE PYROLYSIS OF 2,3-DICHLOROBUTANE

Thesis by

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INTRODUCTION

The importance of butadiene* as a compound of industrial value is becoming more and more realized as the demand for synthetic resins, of widely varying properties, increases. For it has been known for some time that the controlled polymerization of butadiene yields plastics whose properties give rise to many useful applications. In Russia today, butadiene is being produced from the high temperature cracking of ethyl alcohol[2] and "synthetic rubber" is manufactured by polymerization, from the product.

The chief difficulty, however, seems to lie in the fact that to date no industrial method for the synthesis of butadiene has proven economically feasible, for even the Russian "synthetic rubber" is produced at greater cost per pound than the natural product. Although butadiene occurs in gases from petroleum vapor phase cracking (Around 1%) and in the pressure condensate of coal carbonization gases as well as in the pyrolysis products of many organic compounds such as cyclohexane, lower aliphatic alcohols[3], fusel oil[4] and dichlorinated products; its presence is usually characterized by the small percentage found or the effect of larger yields is offset by cost of production.

* 1,3-Butadiene, also known as bi-ordi-vinyl, diethenyl, pyrolylene, vinyl-ethylene, and erythrene.

It therefore seems apparent that the future of the butadiene-plastic field depends greatly upon the success of developing an industrially practical method for producing this diolefin.

Butadiene has been prepared, using phenol as the raw material. This was reduced by the Sabatier method to hexahydrophenol, which when oxidized with nitric acid, yielded adipic acid. This was converted into the amide and treatment of this amide with hypochlorite gave the diamine from which butadiene was produced by exhaustive methylation[5].

Another method converted acetaldehyde into aldol, which when hydrogenated, yielded 1,3-butylene glycol. When the latter was dehydrated, good yields of butadiene are said to have been obtained.[6] Yields of 85 to 90 percent butadiene have been reported as the result of 80 percent of the glycol and 20 percent steam (at a rate of 100 grams per hour per liter of catalyst) at 220°C. being passed over a catalyst of primary sodium phosphate[7].

Harries[8] prepared impure butadiene by dropping 2,3-dibromobutane onto soda-lime in an iron pot at 600°C and Jacobson[9] obtained better results by employing a tube furnace and operating at 530° to 550°c. Use of 1,4-dichlorobutane was made by Muskat and Northrup[10] who obtained

yields of about 30% butadiene by passing the dichloride over soda-lime at 700° to 730°C.

Butadiene has been prepared from 2,3-dichlorobutane by passing the latter over TiO_2 at atmospheric pressure and 300° to 500°C.[11], while Kazanskii and Rafilzon[12] have lately recorded yields of 30 to 40 percent by passing, 2,3-dichlorobutane over $BaCl_2$ at temperatures of 360° to 400°C. In the latter case, difficulty arose from the rapid poisoning of the catalyst by the tar-like products formed.

None of these methods, however, or other schemes to be found reported in the literature for the preparation of butadiene, seemed to be economically sound enough to be applied industrially. This fact and a general interest in organic pyrolysis of this nature served as the animus for the present work.

The choice of the starting material, ie., 2,3-dichlorobutane, was based upon several factors. In the first place this compound is easily prepared from 2-butene which itself is a cheap raw material occurring in abundance. This dichloride was chosen in preference to the dibromo-compound since the former is more economical to prepare. And finally a good supply of 2,3-dichlorobutane was on hand as a result of undergraduate research studying its preparation from n-butyl alcohol. It was hoped that the method could be developed to such a stage that experiments could be carried out on a scale larger than the laboratory work to be described

here, before the time arrived for the submittance of this thesis, but as is often the case with problems dealing with pyrolysis, the mainfold factors involved prevented the realization of this desire.

THE METHOD

The method used was briefly as follows. Twenty-five cubic centimeters of 2, 3-dichlorobutane were passed through a silica tube containing a catalyst composed of $BaCl_2$ on pumice, and heated in an electric furnace, at atmospheric pressure. The runs were made at various temperatures, and the dichloride was added at various rates. The tars and undecomposed dichloride were trapped; the gases of the reaction being freed of HCl by alkali scrubbing, and by passing through soda-lime and finally dried by $CaCl_2$ and collected in an ampoule cooled in a CO_2-alcohol bath. The trapped residues were fractionated to recover unchanged 2,3-dichlorobutane, the HCl liberated was determined as NaCl from the scrubbing tower (only in last four runs), and the yields of crude butadiene were weighed and subsequently analyzed.

MATERIALS

2,3-Dichlorobutane. This compound was prepared as an undergraduate research problem.[13] 2-Butene was generated from n-butyl alcohol and sulfuric acid and this was chlorinated, washed, dried and distilled under reduced pressure. The following table (Table I) gives the boiling range at the pressures used, the densities, and the experimental runs in which the various samples were utilized.

TABLE I

2,3-dichlorobutane	Boiling Range	Pressure	Density	Used in Runs (inc.)
a	59.5-65°C	125mm	$1.112_{4°}^{20°}$	No. 1 -9
b	ca61°C	127mm	$1.110_{4°}^{20°}$	No. 10-20
c	38.5-41.8°C	50mm	$1.107_{20°}$	No. 21-22
d	40.2-42.3°C	50mm	$1.109_{20°}$	No. 23-27

(Beilstein: Handbuch: 2,3-dichlorobutane, $B.P._{760}$= 115-120°C D_{18}= 1.107)

Catalyst. The catalyst was pumice, crushed and screened to -4+8 mesh and treated with $BaCl_2$ (Merck's C.P. $BaCl_2$). Catalyst (a) was prepared by boiling 27g. of pumice in an aqueous solution of $BaCl_2$. The percentage of $BaCl_2$ in the finished product (12.9%) seemed insufficient (see record of run 1 and 2) and the following catalysts were prepared by heating the pumice in a thick paste of water and $BaCl_2$ and drying this in an oven at 110°C for 24 hours and cooling in a dessicator. The more or less solid mass was broken apart and in catalyst (d) this was screened to insure uniformity of size and eliminate fines. The following table (Table II) gives the composition of the four catalysts.

TABLE II

Catalyst	Per Cent $BaCl_2$	Wt. of Catalyst used in tube	Wt of $BaCl_2$ in this Portion
a	12.9	31g	4g
b	60.9	53.8	32.8
c	79.7	50.	39.6
d	45.4	51.8	23.5

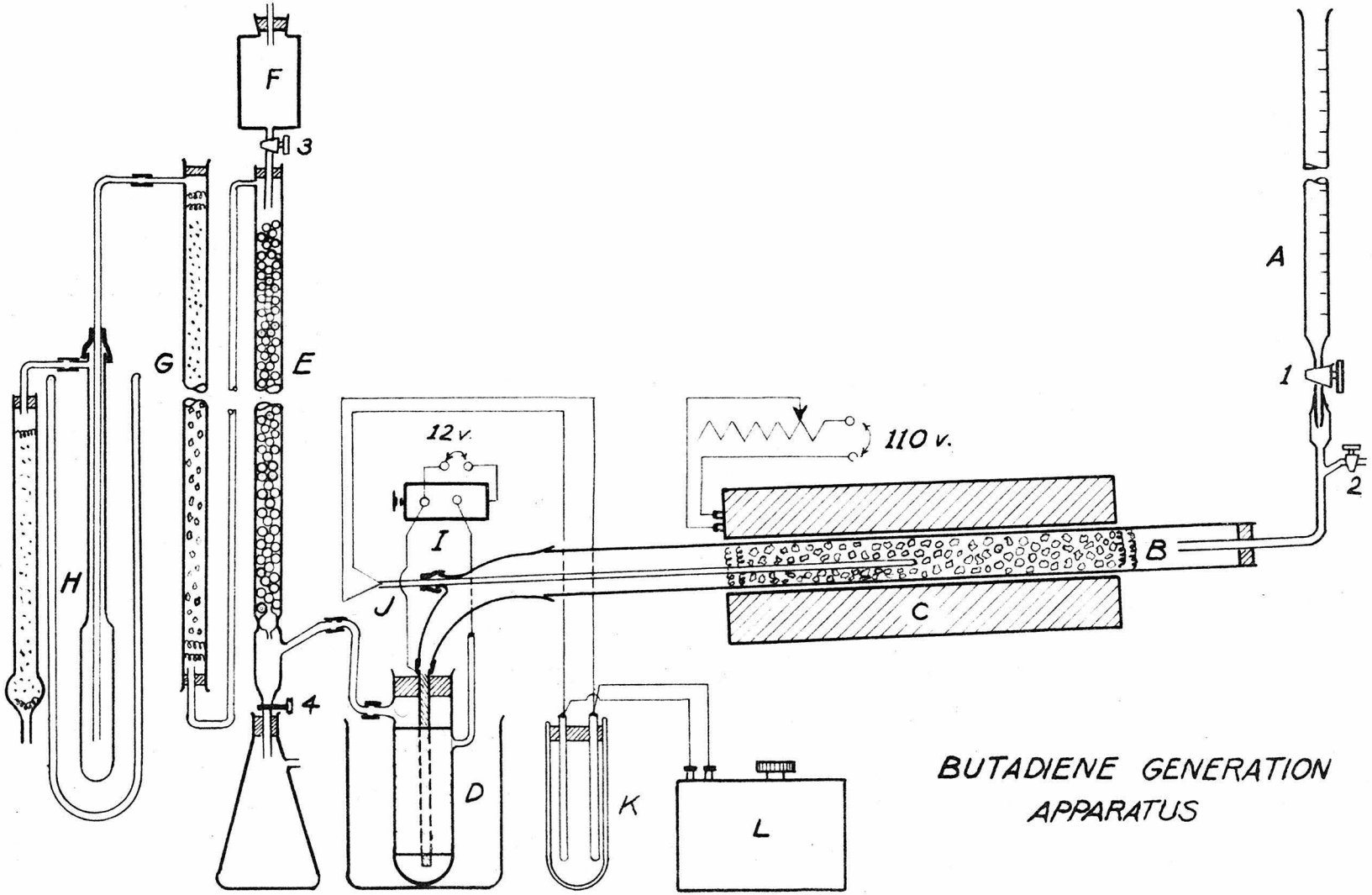
Wash Base. The alkali solution used in the scrubbing tower was approximately 1.5m NaOH. This contained a methyl red-brom thymol blue indicator.

BUTADIENE GENERATION APPARATUS

A diagram of the apparatus is given on the next page. The dichlorobutane was contained in a 50 cc. burette (A) and was run into the pyrolysis tube (B) through the connecting tube. (B) was a silica tube 60 cm in length and 2.2 cm I.D. The feed tube from the burette entered the pyrolysis tube through a rubber stopper. A wick was wrapped around the outside of the tube (B) at this point and the wick ends were placed in water contained in a small porcelain crucible suspended by wire from the tube. The portion of the stopper exposed in the tube was coated with a mixture of asbestos fibre and sodium silicate. The catalyst, held in place by glass wool, was located as shown, in the portion of the tube surrounded by the electric furnace (C).

A Pyrex tube (J) carrying the thermocouple (Chromel-Alumel) wires was inserted into the catalyst. This tube entered the pyrolysis tube through a side arm in the special Pyrex adapter which was sealed onto (B) by means of sealing wax. This seal was also protected by means of a moist wick. The thermocouple leads connected with the cold junction (K) maintained at 0°C, and further to the potentiometer-indicator (L).

The pyrolysis products left (B) through the adapter which was connected to a copper tube extending almost to the



BUTADIENE GENERATION APPARATUS

bottom of trap (D). This trap, surrounded by an ice bath, served as a catch for any liquid products, as well as an electrical precipitator which prevented fog, formed during the run (fog was noticed at rates of dichloride addition exceeding about .45cc per minute), from being carried through the rest of the apparatus. The precipitator consisted of a 20cm. by 3.8cm. test tube with two side arms. An 11cm. sheet of copper was rolled and placed in the tube, serving as the outer electrode. The copper tube carrying the gases from (B) served as the other electrode. The outer electrode was connected to the Ford spark coil (I) (operating on 12 volts D.C.) thru a wire carried by the right side arm; the left side arm serving as the gas outlet.

The gases leaving the trap passed up through bead-filled scrubbing tower (E) (60cm. by 1.7cm.) counter-current to the wash base held in (F), which flowed down. The rate of flow being controlled by cock (3). The neutralized base dropped into a flask as shown. The level of the wash base in the tower was usually kept above the gas inlet by manipulating pinch-clamp (4).

The gases passed from the scrubbing tower up through a tower (G) of similar dimensions whose lower half contained soda-lime, for removing any remaining HCl, and the top portion was filled with $CaCl_2$ for drying the gases.

From the latter the gas was conducted into an ampoule (H) immersed in CO_2-alcohol bath contained in a Dewar flask. The side arm outlet was connected to a $CaCl_2$ tube.

METHOD OF OPERATION

The furnace (C) was turned on; temperature being controlled by the variable rheostat. A stream of dry nitrogen was then passed through the entire apparatus through cock (2) for about ten minutes. This not only cleared the apparatus of any air and moisture, but also eliminated any product from a previous run. During this time the burette (A) was filled with dichlorobutane and the ampoule weighed and connected. When the furnace was at the desired temperature, the cock (2) was closed, precipitator turned on, and the wash base flow adjusted. At a given time the burette stopcock (1) was opened sufficiently to allow the dichloride to flow into the pyrolysis tube. The rate of addition was noted by the number of drops from the burette. After 5cc. had been added, the time elapsed and the temperature of the furnace were recorded. This was repeated at 5cc. intervals until 25cc of dichlorobutane had been added; at which time the cock (1) was closed and cock (2) was opened and a slow stream of N_2 was passed through for about 10 minutes. During the addition the temperature was maintained, as near as was possible, at a constant value. Slight changes in rate of addition caused temperature fluctuation as more heat was required for vaporization and for the reaction itself. While the run was in progress the scrubbing tower was constantly observed, to maintain complete neutralization of the gas. This was made possible by the indicator present in the wash base which was green when basic, yellow when

neutral, and bright red when acid. The wash solution was so adjusted that HCl was taken out by solution as well as neutralization as evidenced by NaCl being "salted out" to some extent.

At the completion of the sweeping with N_2 the ampoule (H), containing the crude butadiene, was disconnected, sealed off and weighed, labeled, and stored in the refrigerator. The residues caught in trap (D) were poured into a weighed vial.

The apparatus as described is found to be fairly satisfactory but considerable technique is required in its operation. Certain changes, it is believed, would alleviate the situation. One of the major difficulties was maintaining a constant rate of dichloride addition since the set-up described operates under a changing pressure head in the burette. Therefore, constant manipulation of the stopcock (1) is necessitated. A constant rate burette would obviate this difficulty. These have been described in the literature[14] and are based on the principle of constant pressure head operating against a constant resistance.

Subsequent analysis of the crude butadiene samples reveals the presence of a comparatively high boiling liquid (Boiling Range 60°-65°) in appreciable percentages and it would therefore seem desirable to eliminate this product to a large extent before the gasses reached the butadiene ampoule. It has been observed that considerable heat is evolved in the scrubbing tower, particularly where the gas enters, and it is suggested that this tower be jacketed and cold water

be passed through the jacket. Since the gases leaving the trap (D) are saturated with the vapor of this higher boiling liquid at least room temperature, the effect of keeping the scrubbing tower cool would tend to condense this liquid since its partial pressure is greatly increased by the removal of the HCl.

As a final improvement in the apparatus, it is suggested that a second ampoule, connected in series with the first (H), be provided and immersed in liquid air. This would collect gases not condensed by the CO_2-alcohol bath and would give a more complete picture of the problem under investigation.

TREATMENT OF THE PRODUCTS

Crude Butadiene

The sealed ampoule of crude butadiene was placed almost immediately after weighing in a tall can and stored in a refrigerator maintained at about 0°-2°C. This kept the product at a low temperature and practically in the dark until it was removed later for analysis. Even after some of the yields had been stored in this way for 14 months, they were clear and colorless at room temperature. However, when they were cooled in this CO_2-alcohol bath prior to opening, a white solid, in small amount, was noticed in the bottom of the ampoule. Storage did not account for this necessarily as the same observation was made directly after several runs, particularly in the case of high rate of butane dichloride addition. This may be water which managed to pass through the drying tower at the higher velocities or perhaps a polymeric substance. Harries reported that butadiene which he had stored in sealed tubes for 5 years had changed to a

white brittle substance. The analysis is described later.

The Residues.

The residues, which were largely mobile blue-green liquids with some tar, collectedin trap (D) and were bottled and weighed. These were later roughly fractionated through a small column at atmospheric pressure chiefly to determine if any of the 2,3-dichlorobutane had passed through the pyrolysis tube undecomposed, and to recover this dichloride.

While a detailed consideration of each fractionation carried out, would be out of place here, as the work was not quantitative, certain observations might be mentioned.

First, fractions recovered from these residues in the neighborhood of 110-118°C were considered as dichlorobutane (BP = 115-120°C). These were obtained in runs No. 1 and No. 2 (See Table III) where the low percentage of $BaCl_2$ in the catalyst proved insufficient to cause complete decomposition of the dichloride. Furthermore, with the higher percentage catalyst,((b) and (c)), dichlorobutane was recovered in all runs made below about 600°C at rates of 2,3-dichlorobutane addition varying from .925 to .521cc per minute. The only run below 600° not showing the dichloride in the residue was No. 4 which, though made at 564°C, had the very slow dichloride addition rate of .197cc per minute.

The second observation was that the larger portion of the first fraction in all the residues came over between 60° and 70°C, with only one exception, ie., No. 8 which was made at 735°, which was the highest temperature investigated. Here the fraction came over at 75°-85°C and further heating

produced no more distillate. The runs having recoverable dichlorobutane produced no further fraction above 118° although the heating bath was raised to 200°. The other runs produced no distillate boiling above about 100°. Apparently if higher boiling constituents were present, they were decomposed. Unstable compounds were indicated in the fractions collected as they went through color changes ranging from pink, blue, green, yellow and finally brown. The characteristic odor of unsaturated compounds was also evident. It is probably that the lower fraction (60°-70°C) was largely composed of chlorobutenes as these were found present in the later analysis of the crude butadiene samples as well, No conclusions were drawn as to the nature of the constituents coming over from 70°-100°C as they represented only a small portion of the residues, nor the residual material in the distilling flask, as pyrolysis of this kind yield complex mixtures of unsaturates and aromatics whose analysis is difficult and here, unimportant.

Since no 2,3-dichlorobutane was discovered in those runs made at temperatures above about 600°, these residue fractionations were not carried out for subsequent runs at such temperatures.

HCl Formed

The HCl formed was determined (in runs No. 24-27) by making the effluent of tower (E) neutral with NaOH and evaporating to dryness and weighing the NaCl. The residue and trap (D) was also washed with water and the washing added to the main solution before neutralizing. The knowledge

of the amount of HCl formed helped as a check on the analysis of the crude yields.

PRELIMINARY RUNS

The first thirteen runs were of an explorative nature. These were made varying the percent $BaCl_2$ in the catalyst, the rate of 2,3-dichlorobutane addition, and the temperature. The record of these runs is given in Table III.

TABLE III

Run	Catalyst	Rate cc/min.	Temp.°C	Grams Residue	Grams Dichloride recovered from residue	Grams Crude Butadiene
1	(a)	.625	605	6.4	3.76	3.4
2	(a)	.521	489	17.2	13.4	2.2
3	(b)	.532	548	4.3	1.4	6.8
4	$(b)_2$	.197	564	4.0 approx.	0.0	7.0
5	$(b)_3$	.338	648	1.6	0.0	8.4
6	$(b)_4$	.926	550	5.8 approx.	3.09	6.0
7	$(b)_5$	.715	608	1.9 approx.	0.0	7.5
8	$(c)_1$	.676 approx.	735	1.2	0.0	6.1
9	$(c)_2$	.582	642	2.5 approx.	0.0	6.0
10	$(c)_3$	.463	645	1.7 approx.	0.0	7.7
11	$(c)_4$	.260	643	4.0 approx.	0.3	6.5
12	$(c)_5$	.281	643	5.0	0.0	6.3
13	$(c)_6$	.510	641	2.45	0.0	6.62

DISCUSSION OF PRELIMINARY RUNS

Effect of Catalyst

The effect of the percent $BaCl_2$ in the catalyst becomes obvious when runs No.1 and 7 are compared. Here the temperatures and rates were essentially the same but run No.

1 was catalyzed by catalyst (a) containing only 4 grams of $BaCl_2$, while run No. 7 usedcatalyst (b) containing 32.8g $BaCl_2$ and yielded 2.2 times as much crude butadiene.

Effect of Temperature

It has been previously noted under the treatment of the residues that complete decomposition of the dichlorobutane did not occur, except at very low addition rates, under about 600°C. Consideration of the yields at temperatures above 600°showed that the highest weights of the crude butadiene occur around 640-650°C. For this reason it was decided to investigate the formation of butadiene in this temperature range, with a catalyst of one composition, and with different rates of dichloride addition.

Effect of Rate

From a superficial examination of the data it would seem that an optimun rate for temperatures around 640° lies somewhere in the neighborhood of .338cc of dichloride a minute. With this catalyst ((b) and (c)), it seems that the crude butadiene yields dropped off slowly with increase in rate from the maximum at .338cc/min., while decreasing the rate seemed to produce the same effect. The purpose of the final runs was to discover an optimun rate with a different catalyst.

However, the work to this point has dealt with the crude yield and it was desired to analyze the products in order to obtain a true picture of the investigation.

ANALYSIS

Analysis of Crude Butadiene

A short water jacket was fitted over the upper end of

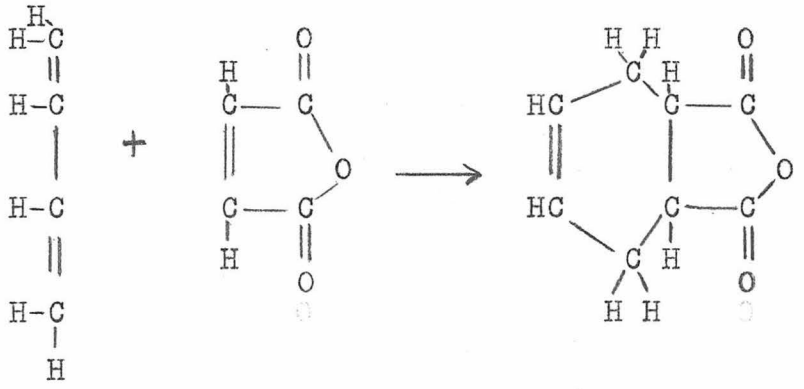
the neck of the butadiene ampoule and when the latter was cooled sufficiently in a CO_2-alcohol bath, it was opened and a thin glass rod, which had been made with fins about 1.5cm. apart and of a diameter small enough to fit into the neck of the ampoule, was quickly inserted and suspended in the neck. The ampoule was then connected to a second ampoule which had been previously cleaned, dried, weighed and cooled in the CO_2-alcohol bath. Ice water was circulated through the jacket and the butadiene was allowed to distill over into the receiving ampoule. The fins on the rod served, in effect, to convert the ampoule neck into a Young fractionating column for separation of the gas from the liquid products present. This scheme obviated the necessity of attaching a separate column to the system and thereby afforded a simple and effective means of separation without the losses accompanying the other method. This fractionation was carried out twice, the distillate residues were weighed and combined for subsequent investigation. The residues obtained on the second distillation were very small, indicating good separation.

The receiving ampoule now contained the gaseous products collected from the pyrolysis and from this an analysis for butadiene was made. A small glass container of about 19cc volume and having a capillary stopcock sealed on it, was evacuated and cooled in the CO_2-alcohol bath. A capillary tube dipping into the condensed butadiene was opened and some of the liquid was allowed to escape in order to drive out air. The end of this tube was then quickly fastened to the end of the inlet of the sample bottle just described,

and the stopcock opened just long enough to suck over a small portion of the liquid. The stopcock was then closed and the sample bottle was connected to the gas burette of the analysis apparatus.

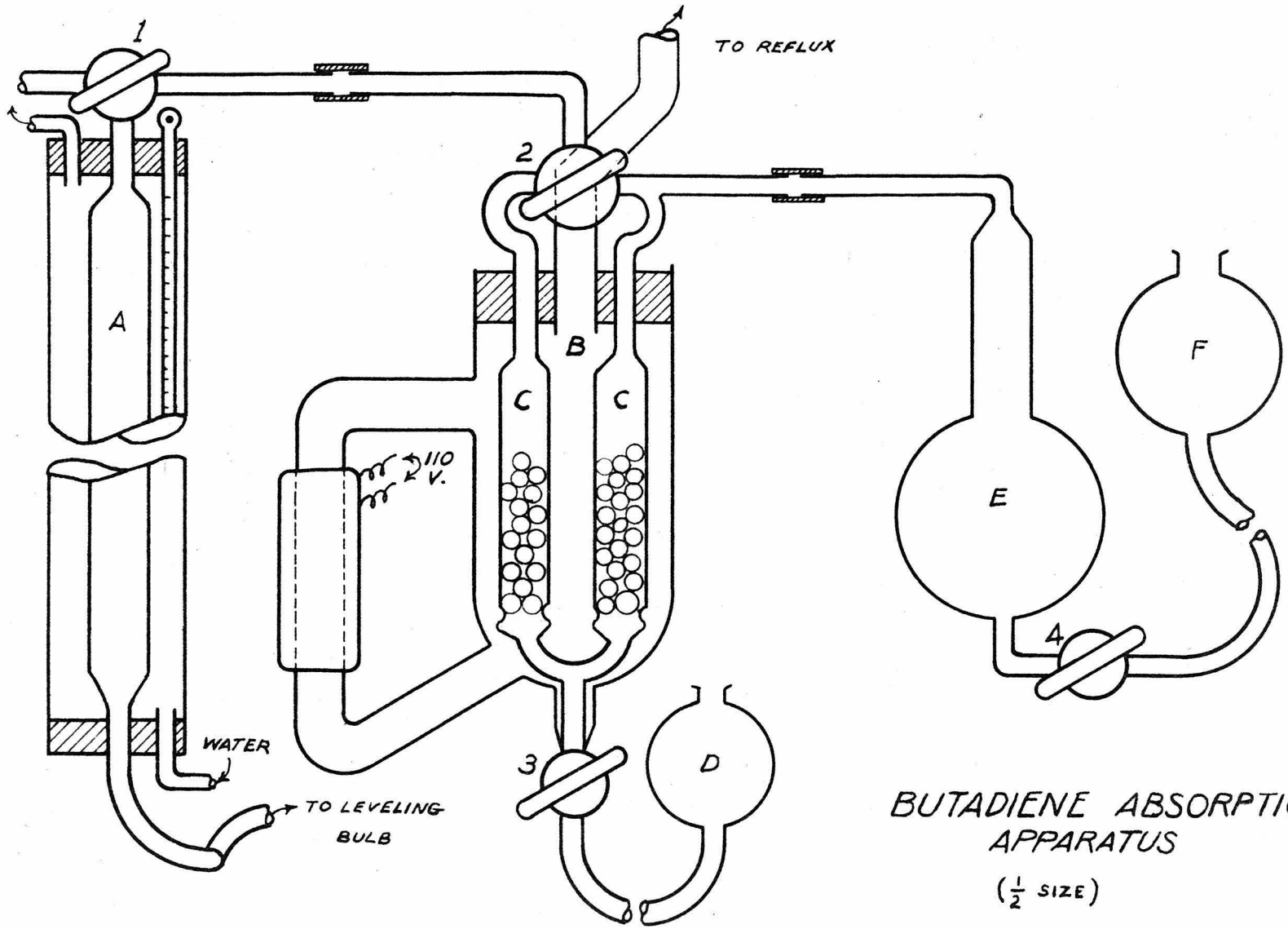
The Analysis Apparatus

The determination of butadiene was based upon the reaction of this gas with molten maleic anhydride according to the equation:



Butadiene — Maleic Anhydride M.P.53° — cis-Δ^4-Tetrahydrophthalic Anhydride M.P.103-104

The apparatus to carry out this reaction was essentially that described by Tropsch and Mattox[15] except that certain modifications were made to adapt it to a gas composed largely of butadiene. The gas burette (A) was water jacketed to maintain constant temperature. This was attached to a leveling bulb filled with a saturated salt solution, colored with methyl red. The T-stopcock (1) connected the burette to the inlet and to the absorption pipette (C) through T-stopcock (2). The absorption pipette was jacketed and the jacket (B) contained water kept at the boiling point by the resistance heater on the sidearm. The water vapor was condensed and returned to the jacket. The pipette was charged with about 8. grams of freshly distilled maleic anhydride through cock



BUTADIENE ABSORPTION APPARATUS

($\frac{1}{2}$ SIZE)

(3) which was attached to a small leveling bulb (D) containing mercury. The pipette cock (2) was connected to gas bulb (E). This bulb was attached to leveling bulb (F) through stopcock (4). The leveling bulb was filled with saturated salt solution.

Operation.

The gas was drawn into burette (A) from the sample bottle, whose contents were completely vaporized, and measured. The gas was then passed down through the left leg and up through the right leg of pipette (C) into gas bulb (E) and then back again to the burette. This was repeated until a constant reading was obtained. The absorption was rapid at first but seemed to drop off logarithmically with successive passes, resulting in a rather slow procedure.

When the constant value had been obtained, the gas was passed through an absorption pipette containing 87 percent H_2SO_4 for removal of n-butenes[16] and any propylene present. Here too the removal was slow. The residual gases were then collected for later investigation.

Residual Gases.

These were analyzed in an apparatus whose construction had just been completed and therefore had not been adequately tested. The combustion was carried out with an excess of O_2 and over a cobalt oxide[17] catalyst. The analysis showed CO_2 as 17.5%, N_2 as 51.9%, and combustibles as 30.6%. The results gave a carbon value for the combustibles of .4 and a hydrogen value of 3.7, obviously not indicating a mixture of hydrocarbons but probably a mixture of H_2 and lower hydro-

-carbons. For the computation of results, the average molecular weight of the gas was taken as 29. which is probably too high, but it affords a factor of safety.

The Distillation Residues

The residues were combined and fractionated at atmospheric pressure (740 mm.). Three fractions were collected. The first fraction boiled at 52. -57.5°, the second fraction at 58.5 -60.9°, and the third fraction at 61.4 - 63.4° C. These fractions decolorized Br_2 in CCl_4 rapidly and gave a precipitate with alcoholic $AgNO_3$, An attempt was made to determine the chlorine quantitatively by treatment with sodium ethoxide and the results showed 26.65 percent Cl. If the fractions were chlorobutenes (39.2% Cl), this would indicate the presence of other constituents in the amount of 32 percent by weight. However, it seems probable that these residues were largely chlorobutenes:

Chlorobutenes	B.P.
$CH_3CCl{:}CHCH_3$	58.5 - 59.°
$CH_3CHClCH{:}CH_2$	64.
$CH_2{:}CClCH_2CH_3$	65. - 66.°

It was previously noted that a liquid of this boiling range was recovered from the trap residue in the preparation procedure. The analysis of the crudes would be greatly simplified if all this material were condensed out by the method suggested under the discussion of the generation apparatus.

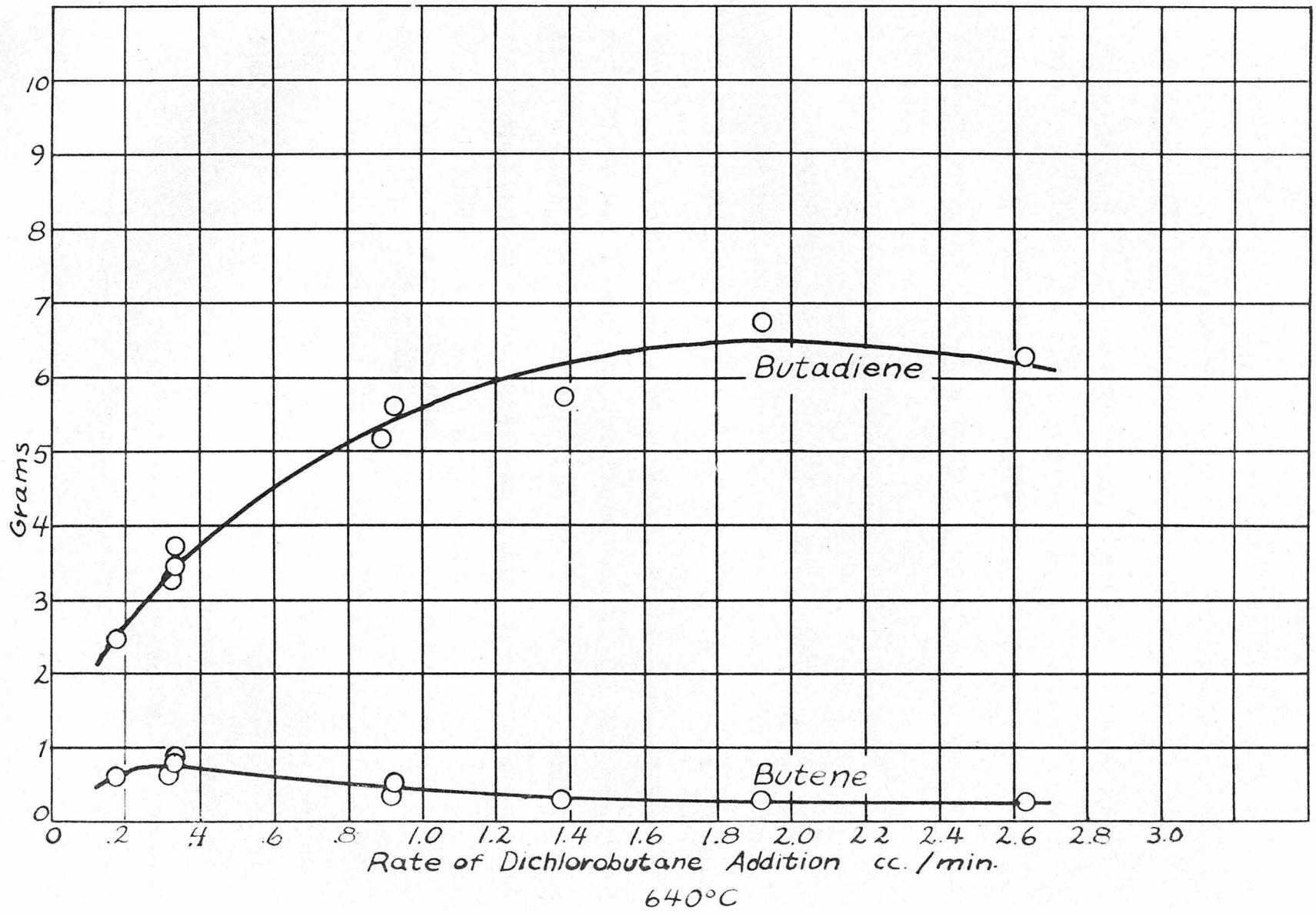
Discussion of Final Runs

Table IV gives the complete data on runs No. 17 to No. 27; runs No. 21 and No. 24 were not recorded owing to mishaps to the apparatus.

Table IV

RECORD AND ANALYSIS OF FINAL RUNS

No.	Catalyst	Temp.°C	Rate cc/ min.	Wt.Trap Residue	Wt.Crude Butadiene	Wt.Dist. Residue	Wt.Dis- tillate	Wt. Butene	Wt. Butadiene	Percent Yield Butadiene
17	$(d)_1$	645	.338	1.8	5.75	1.20	4.55	.914	3.49	29.6
18	$(d)_2$	641	.329	2.5	5.80	1.70	4.10	.651	3.29	28.0
19	$(d)_3$	638	.180	2.4	4.70	1.25	3.45	.626	2.49	21.2
20	$(d)_4$	640	.338	3.1	6.20	1.53	4.67	.797	3.76	32.0
22	$(d)_6$	643	.893	1.8	8.20	1.92	6.28	.513	5.18	43.9
23	$(d)_7$	640	.926	2.4	8.10	1.85	6.25	.377	5.68	48.3
25.	$(d)_9$	643	1.92	1.4	8.70	1.58	7.12	.286	6.78	57.6
26	$(d)_{10}$	639	1.39	1.5+	8.00	1.60	6.40	.291	5.76	49.0
27	$(d)_{11}$	641	2.63	1. +	9.08	2.00	7.08	.288	6.28	53.3


Grams
10
9
8
7
6
5
4
3
2
1
0
Butadiene
Butene
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
Rate of Dichlorobutane Addition cc./min.
640°C

The Catalyst

It will be noted that the same portion of catalyst (d) was used eleven times in succession for these runs and the results certainly indicate that no appreciable poisoning took place as was reported by other investigators[12] using $BaCl_2$. It is possible that the high temperature used here, volatized the tarry substances, which seemed to decrease the catalyst activity, and these collected in the trap. It is also possible that the building up of a catalyst on pumice affects this as well.

HCl Liberated.

In runs No. 25, 26, 27 the amount of HCl neutralized in the scrubbing tower was determined as NaCl. For No. 25 and 27 this corresponded to .374 mols Cl which gives a maximum amount of butadiene in the yield of 10.1g. In No. 26, .354 mols Cl or 9.55g maximum butadiene was found. The discrepancy is accounted for by the presence of the other products. This determination, however, gives an upper limit for butadiene which was not exceeded in the analysis.

Rate of Dichloride Addition

The effect of rate on the formation of butadiene and butene is shown in the plot. However, since these values only apply to the apparatus used, it was thought of value to estimate the actual contact time between the gases and the catalyst. This was done by determining the free space in the catalyst and by computing gas rates assuming that perfect gas laws held, the temperature of the gas was that indicated by the thermocouple, and the pressure was 745 mm. Hg. From these calculations, two contact times

were tabulated. The first set assumed that 3 mols of gas formed ($C_4H_8Cl_2 \rightarrow C_4H_6 + 2HCl$) per mol of dichlorobutane run in and gives a probable upper limit to the velocity or lower limit to the contact time. The second set assumed that only 1 mol of gas formed, i.e., that the dichloride merely vaporized and passed through the catalyst unchanged. This gives an upper limit to the contact time.

Table V

Contact Time in Seconds

	#17	#18	#19	#20	#22	#23	#25	#26	#27
Upper	15.1	15.5	28.4	15.1	5.72	5.52	2.66	3.27	1.94
Lower	5.03	5.16	9.46	5.03	1.91	1.84	.888	1.09	.646

The actual contact time probably lies closer to the lower limit as is substantiated by the analysis of the products obtained.

An examination of the butadiene curve shows definitely that very slow rates decrease the amount found at this temperature. Since the butene found also shows a tendency to decrease the effect is produced either by formation of more chlorobutene or by cracking of the gases to lower hydrocarbons and hydrogen. The latter explanation seems more likely and is somewhat substantiated by consideration of the following totals of products collected from the pyrolysis.

Table VI

Weight of Crude Butadiene and Trap Residue

#17	#18	#19	#20	#22	#23	#25	#26	#27
7.55	8.30	7.05	9.25	10.00	10.50	10.1	10.1	10.5
└Less than .4cc/min				└Greater than .4cc/min.				

It is readily seen that the runs made at the slower rate show a loss which can probably be accounted for by formation of lower hydrocarbons not condensed by the CO_2-alcohol bath. The others seems to be practically constant in the amount lost in this way. A material balance on a run eg. No. 25, shows 10.1g. product and 13.64g HCl formed, totaling 23.74g. The amount put into the system i.e., 25.cc. dichlorobutane is 27.7g. The difference of 3.96g may be due to some carbon remaining in the pyrolysis tube, some of the HCl being in the soda-lime tower, and some loss of residue in transferring, but these factors are undoubtedly small so that at least 3.g or about 10% of non-condensable gases must have been formed during the reaction.

If the trap residues are assumed to be largely chlorobutenes, as their fractionation indicated (at this temperature), then it is seen from the total chlorobutene formed that the maximum yield of this compound occurred at about .338 cc/min. dropping off rapidly with decrease in rate and decreasing more slowly to an apparent constant value as the rate is increased. This fact, together with the observation that the amount of butene formed also approaches an apparent constant value as the rate is increased, would lead one to believe that further increase in rate would not lead to higher yields of butadiene since the loss through cracking, in the last three runs at least, seems more or less constant.

CONCLUSION

It would seem from the foregoing discussion that the method described for the preparation of butadiene from 2,3-dichlorobutane would not be industrially practicable, at least

in the temperature range chosen for the final runs. However, it must be remembered that the catalyst used in these runs was lower in $BaCl_2$ content than the catalysts used in most of the preliminary runs and it is fairly safe to predict that an increase in this content would lead to higher yields. Further, the apparatus used was not as adaptable to the higher velocities owing to difficulty in rate control, but this difficulty can be eliminated as was previously suggested. Decrease in contact time could also be accomplished by shortening the catalyst zone.

Operation at lower temperatures and short contact times might lead to good productive methods, even if all of the dichloride was not decomposed. The undecomposed dichloride could be recovered, and used again and the cracking effects, noted at high temperatures, would be minimized. Temperatures much below 600°C, however, do not seem advisable due to probable high chlorobutene production and catalyst inefficiency due to deposition of tar.

Higher temperatures would undoubtedly increase loss through cracking and probably lead to the formation of other products such as aromatics. In the pyrolysis of lower hydrocarbons it has been noticed that the highest percentage of butadiene found, occurred just below the temperature at which aromatics formed.

The method, on the whole, seems promising, however, as the yields of butadiene have surpassed any found reported in the literature, using dichlorobutane as the starting material, and practically all of the other methods which have any commercial significance.

SUMMARY

1. A satisfactory laboratory apparatus and method for preparing butadiene from 2,3-dichlorobutane, by passing over $BaCl_2$ on pumice, at temperatures ranging from 500-600°C., has been described.
2. An analytical method for the products is developed using maleic anhydride to absorb butadiene, 87 percent sulfuric acid for butenes, and fractional distillation for the separation of chlorobutenes from the butadiene.
3. Butadiene, chlorobutene, butene, lower hydrocarbons, and hydrochloric acid have been shown to result from the pyrolysis of 2,3-dichlorobutane over $BaCl_2$.
4. Conditions are described for obtaining yields, of butadiene as high as 57.6% and optimun conditions are predicted. The higher yields here obtained exceeding those found in the literature, for this pyrolysis.

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References to the Literature

1. Ellis: Petroleum Derivatives, 616, 617, 625-30.

2. J.I.E.C., 28, 4, (April 1936), 395-6

3. Lebedev, Brit. Pat. 331, 482, 1929; Brit. Chem.Abs., B 1930,939.

4. Caventou, Ann., 1863, 127, 93.

5. Harries; Ann., 1911, 383, 179; Chem. Abs., 1911, 5, 3519

6. Kyriakides, J.A.C.S., 1914, 36, 980.

7. Reppe and Hoffman, U.S.Patent, 1,841,055,Jan.12,1932; Chem.Abs. 1932 26 1615

8. Ann. 1911, 383, 176, 181

9. J.A.C.S. 1932, 54, 1545

10. J.A.C.S. 1930, 52, 4050

11. Müller - Conradiand Ober, Chem.Abs,, 1933, 27, 992

12. Chem. Abs., 1935, 29, 3297

13. Skinner, Undergraduate Report on Pre. of 2,3-Dichlorobutane, CI.T., 1934.

14. Corson, J.I.E.C. 6 (July 1934), 297.

15. J.I.E.C.6 (Anal.Ed), 404-5

16. Tropsch and Mattox, ibid, 104-6

17. Walker and Christensen, J.I.E.C. (Anal.Ed.) 7, 9.